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DERWENT-WEEK: 200052

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TITLE: Laminate with good adhesion between layers -  
consisting of metal layer, corrosion resistant layer  
contg. reaction prod. of ionomer and epoxy! cpd. and resin  
coating layer

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APPLICATION-DATA:

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ABSTRACTED-PUB-NO: JP 05286072A

BASIC-ABSTRACT:

Laminate consists of (A) base metallic material, (B) corrosion  
resistant layer  
contg. reactin prod. of ionomer and epoxy cpd. and (C) curing resin  
layer.

(B) is water dispersion compsn. consisting of 100 pts. wt. of ionomer resin and 0.05-50 pts. wt. of water-soluble multivalent epoxy cpd. (C) is one or more of urethane resin, melamine resin and acryl resin.

USE/ADVANTAGE - Used for car parts, electric appliances and building materials.

Adhesions between metal and corrosion resistant layer and adhesion between

corrosion resistant layer and curing resin layer are strong.

In an example, melt ionomer resin which was prepd. by melting partially neutralised ethylene-methacrylic acid copolymer at 250 deg. C was added to water and homogenised to give an ionomer resin water dispersion. To the water dispersion (100g), tetraethylene glycol diglycidyl ether water soln. (1.5g) was added and stirred to give a water dispersion compsn., (A). A 200 micron thick Al foil washed with n-hexane and the water dispersion (A) was bar coated on its surface and burned at 150 deg. C in air oven to give 6 micron thick dry membrane with corrosion resistance. On the membrane, urethane paint was sprayed and burned at 80 deg. C to give a 60 microns thick cured resin layer. The laminate had strong initial adhesion and kept adhesion after waterproof test. It did not rust after waterproof test.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: LAMINATE ADHESIVE LAYER CONSIST METAL LAYER CORROSION RESISTANCE

LAYER CONTAIN REACT PRODUCT IONOMER POLYEPOXIDE COMPOUND RESIN

COATING LAYER

DERWENT-CLASS: A14 A21 A25 A82 G02 M13 P42 P73

CPI-CODES: A10-E01; A12-B04; A12-B07; G02-A05E; M13-H05;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

017 ; R00326 G0044 G0033 G0022 D01 D02 D12 D10 D51 D53 D58 D82 ;  
R00460 G0306 G0271 G0260 G0022 D01 D12 D10 D51 D53 D58 D60 D84

F36

F35 ; S9999 S1025 S1014 ; H0022 H0011 ; P0588 ; M9999 M2415 ;  
H0226

; P1150 ; P0088 ; P0179

Polymer Index [1.2]

017 ; ND01 ; K9574 K9483 ; K9698 K9676 ; B9999 B5301 B5298 B5276  
; Q9999 Q6826\*R ; Q9999 Q7330\*R ; Q9999 Q9289 Q9212

Polymer Index [1.3]

017 ; K9552 K9483

Polymer Index [1.4]

017 ; H0157

Polymer Index [2.1]

017 ; R00952 G1025 G0997 D01 D11 D10 D50 D88 F28 F26 F34 ;  
G1570\*R

G1558 D01 D11 D10 D23 D22 D31 D42 D50 D69 D83 F47 7A ; S9999  
S1616

S1605 ; P0464\*R ; H0022 H0011 ; H0226

Polymer Index [2.2]

017 ; ND01 ; K9574 K9483 ; K9698 K9676 ; B9999 B5301 B5298 B5276  
; Q9999 Q6826\*R ; Q9999 Q7330\*R ; Q9999 Q9289 Q9212

Polymer Index [2.3]

017 ; K9552 K9483

Polymer Index [2.4]

017 ; H0157

Polymer Index [3.1]

017 ; P1592\*R F77

Polymer Index [3.2]

017 ; R00859 G1809 G1649 D01 D23 D22 D31 D45 D50 D83 F19 F10 F07  
; H0011\*R ; P0259\*R P0226

Polymer Index [3.3]

017 ; G0260\*R G0022 D01 D12 D10 D51 D53 ; H0000 ; H0011\*R ; P0088

Polymer Index [3.4]

017 ; ND01 ; K9574 K9483 ; K9698 K9676 ; B9999 B5301 B5298 B5276  
; Q9999 Q6826\*R ; Q9999 Q7330\*R ; Q9999 Q9289 Q9212

Polymer Index [3.5]

017 ; K9712 K9676 ; K9745\*R ; B9999 B4988\*R B4977 B4740

#### POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

Key Serials: 0004 0207 0218 0231 0241 0418 1276 1282 1294 1329 1597  
1601 1737

2001 2020 2022 2504 2509 2691 2737 2829 3173 3252

Multipunch Codes: 017 034 04- 041 046 047 074 075 077 231 24- 250 27&  
397 42&

436 54& 582 597 600 613 623 627 672 724 017 034 038 04- 062 169 170  
199 208 226

27& 336 398 42& 54& 57- 597 600 613 623 627 672 720 017 038 04- 040  
139 150 185

189 231 42& 473 54& 597 600 613 623 627 672

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3. In the drawings, any words are not translated.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention relates to the layered product which has the paint film which is excellent in a water resisting property, and is excellent also in adhesion about a layered product.

[0002]

[Description of the Prior Art] It is known well that ionomer resin, such as a partial neutralization object which comes to neutralize the one section of the carboxyl group which an ethylene-methacrylic-acid copolymer has in a side chain with a metal cation, has various kinds of base materials especially a metal, and good adhesion. Moreover, since the paint film which consists of this ionomer resin is excellent in a water resisting property, using this ionomer resin as a rust-proofer of a metal base is also known.

Furthermore, since ionomer resin can be easily distributed in water, it is known that it can be used as a water dispersing element. Therefore, the rust-proofing layer which applies the water dispersing element containing this ionomer resin to base materials, for example, a steel plate, such as a metal, and consists of ionomer resin is formed, and manufacturing a rust-proofing steel plate is performed.

[0003] By the way, the demand which forms the coat which becomes the rust-proofing steel plate with which use was presented from hardenability resin, such as a coating, further for the purpose of coloring only by applying a rust-proofer to the base of a base material conventionally with diversification and upgrading of the application of a rust-proofing steel plate in recent years has increased.

[0004]

[Problem(s) to be Solved by the Invention] However, the rust-proofing layer which consists of ionomer resin was not able to form good paint, even if adhesion with the paint film which consists of hardenability resin, such as a coating, was bad and carried out the finishing paint of the coating etc. on the paint film of this ionomer resin.

[0005] Then, the purpose of this invention is to offer the layered product which is excellent also in the adhesion of hardenability resin layers, such as a coating formed on the rust-proofing layer, and a rust-proofing layer while having the rust-proofing layer which is excellent in adhesion with a water resisting property, a metal, etc.

[0006]

[Means for Solving the Problem] In order to solve said technical problem, this invention offers the layered product which has the rust-proofing layer (B) which uses the reactant of a metal base (A), and an ionomer resin and an epoxy group content compound as a principal component, and the hardenability resin layer (C) by which the laminating was carried out on the metal base (A) through said rust-proofing layer (B).

[0007] It is desirable in it being what the reactant (B) of said ionomer resin and an epoxy group content compound becomes from the water nature powder body composition object containing the ionomer resin 100 weight section, and the water-soluble multiple-valued epoxy group content compound 0.05 - 50 weight sections.

[0008] Said hardenability resin layer (C) is desirable in it being what consists of at least one sort chosen from urethane resin, melamine resin, and acrylic resin.

[0009] Hereafter, the layered product of this invention is explained to a detail.

[0010] The layered product of this invention has a metal base (A), and a rust-proofing layer (B) and the hardenability resin layer (C) by which the laminating was carried out on the metal base (A) through the rust-proofing layer (B). The laminating of a rust-proofing layer (B) and the hardenability resin layer (C) may be carried out to one side of a metal base (A), and the laminating may be carried out to both sides of a metal base (A).

[0011] In the layered product of this invention, the metal plate which especially a metal base (A) is not restricted, for example, consists of metallic elements, such as aluminum, iron, copper, nickel, and zinc, or an alloy plate is mentioned. Moreover, the thing to which surface treatment may be carried out and polish processing, plating, etc. are performed for example, which is sufficient as a metal base (A).

[0012] The configuration of this metal base (A), a dimension, thickness, etc. are suitably chosen according to the application of the layered product of this invention etc.

[0013] Moreover, a rust-proofing layer (B) uses the reactant of ionomer resin and an epoxy group content compound as a principal component, and is usually formed from the water nature powder body composition object containing ionomer resin (b1) and a water-soluble multiple-valued epoxy compound (b2).

[0014] The ionomer resin which is the component (b1) of a water nature powder body composition object consists of a giant-molecule principal chain which mainly consists of hydrocarbons, it has a carboxyl group in a side chain, and the at least 1 section of this carboxyl group is the polymer neutralized with the metal cation. As an example of this ionomer resin, it is the copolymer of ethylene and unsaturated carboxylic acid, and the partial neutralization object which comes to neutralize the at least 1 section of the carboxyl group to contain with a metal cation is mentioned. A random copolymer is sufficient, the graft copolymer of the unsaturated carboxylic acid to polyethylene is sufficient as the ethylene-unsaturated-carboxylic-acid copolymer which constitutes the main frame of this ionomer resin, and its random copolymer is desirable in respect of transparency.

[0015] As unsaturated carboxylic acid which is the component of an ethylene-unsaturated-carboxylic-acid copolymer, the unsaturated carboxylic acid of carbon numbers 3-8 etc. is mentioned. As an example of the unsaturated carboxylic acid of these carbon numbers 3-8, an acrylic acid, a methacrylic acid, a maleic acid, boletic acid, an itaconic acid, a crotonic acid, isocrotonic acid, a citraconic acid, an allyl compound succinic acid, mesaconic acid, glutaconic acid, a NAJIKKU acid (the endo-cis-bicyclo [2, 2, 1] hept-2-en -5, 6-dicarboxylic acid), a methyl NAJIKKU acid, a tetrahydro FUTARU acid, methyl hexahydrophthalic acid, etc. are mentioned. Also in these, a methacrylic acid is desirable especially.

[0016] Moreover, in addition to ethylene and unsaturated carboxylic acid, the ethylene-unsaturated-carboxylic-acid copolymer which constitutes the main frame of this ionomer resin (b1) may contain the 3rd component. As this 3rd component, vinyl ester, such as unsaturated-carboxylic-acid ester, such as a methyl acrylate (meta), an ethyl acrylate (meta), and isobutyl acrylate (meta), and vinyl acetate, is mentioned.

[0017] The content of the ethylene in this ethylene-unsaturated-carboxylic-acid copolymer is 95 - 60 % of the weight, and is usually 92 - 75 % of the weight preferably. Moreover, the content of unsaturated carboxylic acid is 5 - 40 % of the weight, and it is usually desirable that it is in 8 - 25% of the weight of the range especially. Moreover, when an ethylene-unsaturated-carboxylic-acid copolymer contains the 3rd component, as for the 3rd component, it is desirable to exist in 40 or less % of the weight of an amount.

[0018] In the ionomer resin (b1) of this invention, it is the point that the ionomer resin which a 1 - trivalent metal cation is mentioned and has good emulsifiability, for example as a metal cation with which the ethylene-unsaturated-carboxylic-acid copolymer is neutralizing a part of carboxyl group [ at least ] which it has in a side chain is obtained, and a univalent metal cation is desirable. Also in this univalent metal cation, sodium and a potassium are desirable especially.

[0019] It is the point that the water dispersing element which has good stability is obtained, and

whenever [ rate / that the ethylene-unsaturated-carboxylic-acid copolymer was neutralized by the metal cation to all the carboxyl groups that it has in a side chain / of a carboxyl group /, i.e., neutralization, ] is about 20 - 100%, and is usually about 30 - 80% preferably while excelling in the adhesion of a paint film.

[0020] This ionomer resin (b1) is ASTM. D That whose MFRs (190 degrees C) by 1238 are 0.05-100g / 10min is desirable, and what is 0.1-50g / 10min is especially desirable.

[0021] Manufacture of this ionomer resin (b1) carries out copolymerization of said 3rd component by the high-pressure radical polymerization method ethylene, unsaturated carboxylic acid, and if needed, it can carry out the graft copolymerization of the unsaturated carboxylic acid to the approach and the polyethylene which carries out neutralization processing, and the compound which has said metal cation for the carboxyl group of the copolymer obtained can perform it according to approaches, such as the approach of carrying out neutralization processing, with the compound which has said metal cation for the carboxyl group of the ethylene-unsaturated-carboxylic-acid copolymer obtained. Moreover, melting kneading may be supplied and carried out, and this manufacture may make a necessary component react to an extruder, and may be made to react in a suitable solution.

[0022] Moreover, the glycidylethers obtained by a reaction with the metal alkoxide of the glycidyl ester obtained by reactions, such as a carboxylic acid and 2 and 3-epoxy propanol, and epichlorohydrin, univalent, or many \*\* etc. as an epoxy group content compound which is the component (b2) of a water nature powder body composition object can be mentioned.

[0023] As a carboxylic acid for obtaining glycidyl ester For example, saturation monocarboxylic acid, such as an acetic acid, a propionic acid, butanoic acid, and a valeric acid; A malonic acid, Saturation dicarboxylic acid, such as a succinic acid, a glutaric acid, and an adipic acid; A benzoic acid, Aromatic carboxylic acid, such as a phthalic acid; Partial saturation monocarboxylic acid, such as an acrylic acid and a methacrylic acid, A maleic acid, boletic acid, an itaconic acid, a crotonic acid, isocrotonic acid, a citraconic acid, an allyl compound succinic acid, mesaconic acid, glutaconic acid, and a NAJIKKU acid (the endo-cis-bicyclo [2, 2, 1] hept-2-en -5 and 6-dicarboxylic acid --) Partial saturation dicarboxylic acid, such as a methyl NAJIKKU acid, a tetrahydrophthalic acid, and methyl hexahydrophthalic acid, is mentioned. Independent one sort or two or more sorts of combination of these carboxylic acids may be included in glycidyl ester.

[0024] As an example of the glycidyl ester used as an epoxy group content compound (b2), adipic-acid diglycidyl ester, phthalic-acid diglycidyl ester, terephthalic-acid diglycidyl ester, etc. are mentioned.

[0025] The metal alkoxide of univalent [ for obtaining the glycidylethers used as an epoxy group content compound (b2) ] or many \*\* is a compound obtained by the reaction of the alcohol of univalent or many \*\*, and a metal. As univalent alcohol, a methanol, ethanol, propanol, a butanol, a hexanol, etc. are mentioned and polyhydric alcohol, such as ethylene glycol, resorcinol, and a glycerol, etc. is mentioned as polyhydric alcohol, for example. As a metal, alkali metal or alkaline earth metal, such as a lithium, sodium, a potassium, magnesium, and calcium, etc. are mentioned, for example.

[0026] Sodium alcoholate etc. is mentioned as an example of the metal alkoxide of univalent [ this ] or many \*\*. Independent one sort or two or more sorts of combination of these metal alkoxides may be included in glycidylethers.

[0027] As an example of the glycidylethers used as an epoxy group content compound (b2) Sorbitol polyglycidyl ether, sorbitan poly glycidyl ether, Polyglycerol polyglycidyl ether, pentaerythritol polyglycidyl ether, Diglycerol polyglycidyl ether, glycerol polyglycidyl ether, Trimethylolpropane polyglycidyl ether, neopentyl glycol diglycidyl ether, Ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, A propylene glycol diglycidyl ether, polypropylene-glycol-diglycidyl-ether, 2, and 2-bis(4'-glycidyoxy phenyl) propane etc. is mentioned.

[0028] Moreover, the water nature powder body composition object may contain said glycidyl ester and glycidylethers as an epoxy group content compound (b2) combining independent one sort or two sorts or more.

[0029] This epoxy group content compound (b2) is the point which forms the paint film which reacted with the carboxyl group of ionomer resin (b1) with heating, and was excellent in adhesion with the after-

mentioned hardenability resin layer (C), and its multiple-valued epoxy group content compound of diglycidyl ether, such as ethylene and polyethylene glycol diglycidyl ether, is especially desirable.

[0030] Moreover, this epoxy group content compound (b2) is the point that preparation of a water nature powder body composition object becomes easy, what forms water solubility or dispersion is desirable, and 25% or more of water-soluble thing has especially desirable water soluble ratio. In this invention, water soluble ratio means the rate of the amount of the epoxy group content compound (b2) which actually dissolved in water, when an epoxy group content compound (b2) is mixed in water at 25 degrees C. That is, when epoxy group owner compound (b2) A1 g is dissolved in water at a certain temperature T and the insoluble matter of an epoxy group content compound (b2) A2 g Remains, the water soluble ratio of the epoxy group content compound (b2) in temperature T becomes  $[(A1-A2)/A1] \times 100(\%)$ . For example, when 10g (b2) of epoxy group content compounds is mixed in 90g of water and 3g (b2) of insoluble epoxy group content compounds remains, it becomes 70% of water soluble ratio.

[0031] Furthermore, as for especially the viscosity of this epoxy group content compound (b2), it is desirable that there is 5-30000cps in the range of 10-20000cps at 25 degrees C.

[0032] In this invention, that to which especially an epoxy group content compound (b2) usually has 80-2500g of weight per epoxy equivalent in the range which is 120-2000g is used. In this invention, weight per epoxy equivalent means the number of grams of the epoxy group content compound per 1 gram equivalent epoxy group. For example, when the epoxy group content compound of molecular weight 100 has one epoxy group in 1 intramolecular, the weight per epoxy equivalent of this epoxy group content compound is set to 100. Moreover, when the epoxy group content compound of molecular weight 100 has two epoxy groups in 1 intramolecular, the weight per epoxy equivalent of this epoxy group content compound is set to 50.

[0033] Moreover, preparation of a water nature powder body composition object can carry out heating fusion of the approach of dissolving an epoxy group content compound (b2) in the water dispersing element of ionomer resin (b1), the approach of mixing the water solution of an epoxy group content compound (b2) to the water dispersing element of ionomer resin (b1), ionomer resin (b1) and an epoxy group content compound (b2), and the mixture of water, and can be performed according to the approach of carrying out package emulsification etc.

[0034] The water dispersing element of ionomer resin (b1) can be prepared easily, can mix the ionomer resin (b1) of 1 - 60% of the weight of the amount of solid content to water, and can usually prepare it by the approach of carrying out heating fusion and distributing at the temperature of 100-270 degrees C.

[0035] Moreover, the ionomer resin in a water nature powder body composition object (b1) and especially the concentration of an epoxy group content compound (b2) are not restricted, but are suitably adjusted according to the method of application, the equipment used for paint. Usually, it is the total quantity of ionomer resin (b1) and an epoxy group content compound (b2), and it is suitable that it is 10 - 40 % of the weight preferably five to 50% of the weight.

[0036] Furthermore, although the content rate of ionomer resin (b1) and an epoxy group content compound (b2) changes in a water nature powder body composition object with the molecular weight of the epoxy group content compound (b2) to be used, weight per epoxy equivalent, etc. While applying a water nature powder body composition object to a metal base (A) and excelling in a water resisting property In that the rust-proofing layer (B) which is excellent in adhesion with top coat is obtained, the ionomer resin (b1) 100 weight section is received. The rate of the epoxy group content compound (b2) 0.05 - 50 weight sections is desirable still more desirable, and the rate of 0.1 - 30 weight section, especially 0.5 - 10 weight section is desirable.

[0037] Moreover, this water nature powder body composition object may contain other components, such as various kinds of resin and a compounding agent, in the range which does not spoil the purpose of this invention if needed in addition to said ionomer resin (b1) and an epoxy group content compound (b2). Water-soluble amino resin for raising the reinforcement of paint films, such as water-soluble melamine resin and water-soluble benzoguanamine resin, as other components, for example; Polyvinyl alcohol, A polyvinyl pyrrolidone, polyvinyl methyl ether, polyethylene oxide, Polyacrylamide, polyacrylic acid, a carboxymethyl cellulose, The stability of a water nature powder body composition



object, such as methyl cellulose and hydroxyethyl cellulose, is raised. The organic thickener for adjusting viscosity; Inorganic thickener; Nonion system surfactants, such as a silicon dioxide, activated clay, and a bentonite, In addition to this, Water-soluble polyvalent metallic salt, such as strontium chromate for raising the rust-proofing capacity of the rust-proofing layer (B) for raising the stability of water nature powder body composition objects, such as an anion system surfactant, surfactant; Obtained; A rust-proofer; antifungal agent; ultraviolet ray absorbent; heatproof stabilizer; foaming agent; titanium white, Pigments, such as red ochre, a phthalocyanine, carbon black, and permanent yellow; A calcium carbonate, Bulking agents, such as a magnesium carbonate, a barium carbonate, talc, an aluminum hydroxide, a calcium sulfate, a kaolin, a mica, asbestos, a mica, and a calcium silicate, etc. are mentioned.

[0038] It is suitable for the viscosity of this water nature powder body composition object from the viewpoint of the paint workability for forming a rust-proofing layer (B) that it is [ about 30-1000cps ] 50-800cps preferably.

[0039] In the layered product of this invention, formation of a rust-proofing layer (B) is performed by applying said water nature powder body composition object on a metal base (A), and making it dry and harden. Spreading of a water nature powder body composition object can be performed by approaches, such as a spray, a curtain, a flow coater, a roll coater, brush coating, and immersion. After applying a water nature powder body composition object, it is desirable to burn, although you may make it season naturally. Printing temperature is 80-250 degrees C, and a good rust-proofing layer (B) is formed by heating for [ 20 seconds - ] 10 minutes. In the formation process of this rust-proofing layer (B), since most water nature powder body composition objects are what does not contain an organic solvent etc., they have the advantage which can keep good the work environment in that production process.

[0040] The thickness of a rust-proofing layer (B) is suitably chosen according to the class of hardenability resin for forming the application of a layered product, the water nature powder body composition object to be used, and the after-mentioned hardenability resin layer (C), the thickness of a hardenability resin layer (C), etc., and is not limited especially. Usually, in order to demonstrate sufficient rust-proofing ability, without producing a paint film crack after applying a water nature powder body composition object when it dries, the thickness of 1-10 micrometers is especially desirable 0.5-20 micrometers.

[0041] The hardenability resin layer (C) of the layered product of this invention is formed on said rust-proofing layer (B), and consists of hardenability resin of a heat hardening mold or a room-temperature-setting mold. As hardenability resin used, the coating which consists of acrylic resin, an acrylic denaturation alkyd resin, an epoxy resin, urethane resin, melamine resin, phthalic resin, amino resin, polyester resin, vinyl chloride resin, etc. is mentioned, for example. Also in these, as a hardenability resin layer (C), since especially adhesion with a rust-proofing layer (B) is excellent, urethane resin, melamine resin, or acrylic resin is desirable.

[0042] Moreover, this hardenability resin may contain rust preventive pigments, such as metal pigments, such as extenders, such as color pigments, such as a titanium white and carbon black, and talc, aluminium powder, and copper powder; a minium, and a lead sulfate, etc. Furthermore, a dispersant, a drying agent, a plasticizer, a defoaming agent, a thickener, a stabilizer, an anti-skinning agent, an antimold, antiseptics, an antifreezing agent, etc. may be contained.

[0043] In the layered product of this invention, according to the application of a layered product, the class of hardenability resin to be used, etc., the thickness of a hardenability resin layer (C) is determined suitably, and is not restricted especially. Usually, about 5-300 micrometers is about 10-200 micrometers especially preferably.

[0044] In the layered product of this invention, on a rust-proofing layer (B), formation of a hardenability resin layer (C) applies and heats hardenability resin, can be dried, can be stiffened, and can be performed. The drying time and temperature are suitably adjusted according to the class of hardenability resin applied, the thickness of a hardenability resin layer (C), etc. Usually, especially, it is about 20 - 80 minutes, and hardening is completed in about one week by the hardenability resin of a room-temperature-setting mold for 5 to 120 minutes. The range of drying temperature is ordinary temperature

-200 degree C, and the range of it is usually 50-150 degrees C especially.

[0045] By the rust-proofing layer (B), since it excels in a water resisting property and rust-proofing nature, the layered product of this invention can be suitably used as autoparts, household electric appliances, building materials, etc. Furthermore, since the paint film which consists of the rust-proofing layer (B) and hardenability resin layer (C) of this layered product is excellent also in draw-forming nature, surface-protection nature, and heat-sealing nature, the layered product of this invention can also be used for the various purposes taking advantage of these properties.

[0046]

[Example] Although an example is given and this invention is explained concretely hereafter, this invention is not restricted at all by these examples. In addition, in the following examples, evaluation of a paint film was performed by the following approaches.

[0047] Initial paint film adhesion (cross cut adhesion test)

JIS After creating the test piece which attached the squares according to the approach of the cross cut adhesion test indicated by K5400 and sticking adhesive tape (the Nichiban [ Co., Ltd. ] make, a trade name: Scotch tape) on the squares of a test piece, the number of the squares which adhesive tape was made to pull and exfoliate in the 90-degree direction promptly, and did not exfoliate among the squares 100 was counted, and the value of the (number of the squares which did not exfoliate) / 100 was made into the index of adhesion.

[0048] Adhesion after a water resistant test: After the test piece was immersed in 40-degree C brine (3 % of the weight) for 200 hours, the above-mentioned cross cut adhesion test was performed.

[0049] The rate of rusting: After presenting the above-mentioned water resistant test with the test piece of 10cm angle, % showed the area which rust generated on the front face of a test piece.

[0050] (Example 1)

(Preparation of a water dispersing element) 100g (MFR(190 degrees C) 0.8g whenever [ /10min, 15 % of the weight / of methacrylic-acid contents /, and neutralization ] 50%, a neutralizer : sodium hydroxide) of ethylene-methacrylic-acid copolymers neutralized partially was fused at 250 degrees C, and ionomer resin melt was prepared. It inserted in the proof-pressure homomixer of 1l. of content volume which inserted in 300g of water and heated this ionomer resin melt at 170 degrees C over about 2 hours, agitating by 1000rpm. It cooled to the room temperature, agitating for 30 more minutes, and the water dispersing element of ionomer resin was obtained. The resin concentration of the water dispersing element of the obtained ionomer resin was [ 600cps (25 degrees C) and mean particle diameter of viscosity ] 1 micrometer or less 25% of the weight. Next, 50% of the weight of the water solution of tetraethylene glycol diglycidyl ether was prepared, to 100g of water dispersing elements of ionomer resin, 1.5g added, this water solution was agitated, and the water nature powder body composition object (henceforth "the water nature powder body composition object A") was obtained.

[0051] (Paint) After applying the above-mentioned water dispersing element A to the front face of the aluminum foil (thickness: 200 micrometers) washed by n-hexane by the bar coating machine so that it may be set to 6 micrometers by desiccation thickness, printing processing was performed on it at 150 degrees C in air oven for 5 minutes, and the rust-proofing layer was formed in it. Furthermore, on the rust-proofing layer, the urethane coating (the Kansai Paint Co., Ltd. make, RETAN PG 60) was painted so that it might become the thickness of 60 micrometers by the spray, among air oven, printing processing was performed for 30 minutes at 80 degrees C, the hardenability resin layer was formed, and the paint sample was produced. About this paint sample, initial paint film adhesion (cross cut adhesion test) and the adhesion after a water resistant test were evaluated, and the rate of rusting was measured. A result is shown in Table 1.

[0052] (Example 2) replace a coating with a melamine coating (the Nippon Paint Co., Ltd. make, ORUGA selection), and be burned -- except having changed conditions into the conditions shown in Table 1, the paint sample was produced like the example 1, and initial paint film adhesion (cross cut adhesion test) and the adhesion after a water resistant test were evaluated, and the rate of rusting was measured. A result is shown in Table 1.

[0053] (Example 3) Except having replaced the epoxy group content compound with 2 and 2-bis(4'-

glycidyoxy phenyl) propane diglycidyl ether, the paint sample was produced like the example 1, and initial paint film adhesion (cross cut adhesion test) and the adhesion after a water resistant test were evaluated, and the rate of rusting was measured. A result is shown in Table 1.

[0054] (Example 4) Except having added 15g of 50% of the weight of water solutions of tetraethylene glycol diglycidyl ether to 100g of water dispersing elements of ionomer resin, having prepared the water dispersing element, and having used this water dispersing element, to the water dispersing element of ionomer resin, the paint sample was produced like the example 1, and initial paint film adhesion (cross cut adhesion test) and the adhesion after a water resistant test were evaluated to it, and the rate of rusting was measured to it. A result is shown in Table 1.

[0055] (Example 1 of a comparison) Only using the water dispersing element of the ionomer resin adjusted in the example 1, the paint sample was produced like the example 1 and initial paint film adhesion (cross cut adhesion test) and the adhesion after a water resistant test were evaluated. A result is shown in Table 1.

[0056] (Example 2 of a comparison) Only 50% of the weight of the water solution of the tetraethylene glycol diglycidyl ether adjusted in the example 1 was applied, the paint sample was produced like the example 1, and initial paint film adhesion (cross cut adhesion test) and the adhesion after a water resistant test were evaluated. A result is shown in Table 1.

[0057] (Example 5) Except using a cold rolled steel plate (dull finish, thickness: 1mm) instead of aluminum foil, the paint sample was produced like the example 1, and initial paint film adhesion (cross cut adhesion test) and the adhesion after a water resistant test were evaluated, and the rate of rusting was measured. A result is shown in Table 1.

[0058] (Example 3 of a comparison) Only using the water dispersing element of the ionomer resin adjusted in the example 1, except using a cold rolled steel plate (dull finish, thickness: 1mm) instead of aluminum foil, the paint sample was produced like the example 1 and initial paint film adhesion (cross cut adhesion test) and the adhesion after a water resistant test were evaluated. A result is shown in Table 1.

[0059]

[Table 1]

表 1

|       | エポキシ基<br>含有化合物<br>(重量部) *1 | 塗 料     | 焼 付 け 条 件     | 初 期<br>密 着 性 | 耐水後<br>密着性 | 発錆率 |
|-------|----------------------------|---------|---------------|--------------|------------|-----|
| 実施例 1 | 3                          | レタンPG60 | 80°C×30 min   | 100/100      | 100/10     | 0%  |
| 実施例 2 | 3                          | オルガセレクト | 130 °C×15 min | 100/100      | 100/10     | 0%  |
| 実施例 3 | 3                          | レタンPG60 | 80°C×30 min   | 100/100      | 100/10     | 0%  |
| 実施例 4 | 30                         | レタンPG60 | 80°C×30 min   | 100/100      | 100/10     | 0%  |
| 実施例 5 | 3                          | レタンPG60 | 80°C×30 min   | 100/100      | 100/10     | 0%  |
| 比較例 1 | 0                          | レタンPG60 | 80°C×30 min   | 0/100        | —          | —   |
| 比較例 2 | —                          | レタンPG60 | 80°C×30 min   | 0/100        | —          | —   |
| 比較例 3 | 0                          | レタンPG60 | 80°C×30 min   | 0/100        | —          | —   |

注\*1：アイオノマー樹脂100重量部に対するエポキシ基含有化合物の含有割合

[0060]

[Effect of the Invention] The layered product of this invention is excellent also in the adhesion of hardenability resin layers, such as a coating formed on the rust-proofing layer, and a rust-proofing layer while having the rust-proofing layer which is excellent in adhesion with a water resisting property, a metal, etc.

[Translation done.]